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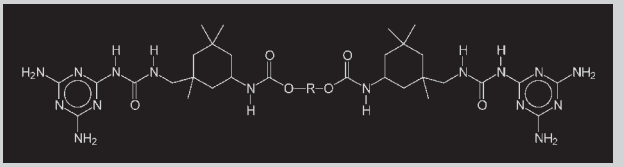
Full Paper: The properties of melamine based supramolecular compounds have been studied with rheological, thermal, mechanical, dielectric and scattering techniques and compared with similar covalently bonded materials. The complexes are based on a linear pTHF-diol ($\bar{M}_n = 1\,000$) connected via a diisocyanate with melamine. The results obtained show that, despite of the material's low molecular weight ($< 2\,000$ g · mol^{-1}), it has properties typical for high molar mass polymers. The material has a high modulus above the glass transition temperature, and shows behavior similar to a semi-crystalline material. This is attributed to the presence of the hydrogen bonds, in combination with phase separation giving rise to hard domain formation. In comparison with a covalently bonded and a low molecular weight material of similar composition, the supramolecular compounds have a higher and more temperature dependent viscosity. By exchanging parts of the pTHF with a low molecular weight diol, in our case hexane diol, the mechanical properties at room temperature could be modified to a stiffer but more brittle material.



Synthesis, Structure and Properties of Melamine-Based pTHF-Urethane Supramolecular Compounds

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Introduction

After the early work of Staudinger it became clear that polymeric properties are the result of the macromolecular nature of the molecule. A large number of repeating units are covalently linked into long chains and the entanglements of the macromolecular chains are responsible for the many typical polymer properties.[1] Entanglements are also causing high viscoelastic behavior in the melt[2] and this hampers polymer processing substantially. It is still open to discussion whether the covalent bonds in macromolecules are inextricable in co-existence with superb mechanical properties of polymers or that new polymers architectures can refute these principles.

Inspired by nature, Lehn[3] pioneered the field of supramolecular chemistry. Supramolecular chemistry deals with the organization of molecules into larger structures via spontaneous assembly by non-covalent interactions.[4] Despite the weakness of non-covalent interactions, thermodynamically stable complex structures can be obtained by cooperative action of several of these weak interactions. For example, low molecular weight compounds, containing well-defined complementary hydrogen bond donor and acceptor units ordered in a controlled way, can associate into polymer like aggregates.[5] However, the strength of these hydrogen donor-acceptor units in the associating pairs was not sufficient to obtain a high extent of association necessary for high molecular weight polymers.

Stadler et al.[6] illustrated the impact of weak hydrogen bonds in urazole-modified polybutadiene. Their results indicated that in particular the rheology is substantially affected by these unstructured hydrogen bonds. The viscoelastic properties of the modified materials responded to the WLF character of polymers.

Meijer and co-workers designed self-complementary donor-donor-acceptor-acceptor (DDAA) units based on ureidopyrimidinone that demonstrated the highest association constants up till now.[7] These units – based on the principles described by Jorgensen[8] were designed to maximize the attractive and minimize the repulsive forces. The rheology of tri-functional low molecular weight compounds provided with ureidopyrimidinone groups were studied and it was found that in the melt, these compounds behaved as networks and the properties resembled those of covalently crosslinked materials.[9] In addition, linear supramolecular polymers were prepared by association of oligomers end-capped with quadruple hydrogen bond forming units, and compared with the corresponding

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oligomers without hydrogen bonding units.[10] A similar rheological behavior was reported of supramolecular materials based on imide functional oligomers and melamine.[11] It was clearly shown in all these cases that these low molecular weight materials possess the rheological behavior that is in general only found by high molecular weight polymers.

Reptation, the most important mechanism of stress relaxation for conventional polymer melts as has been described by de Gennes[12] and Doi and Edwards,[13] may be operative in supramolecular polymers as well. In these reversible polymers, however, an additional stress relaxation mechanism is possible due to the dissociation-association mechanism of the hydrogen bonds.

Thus, there is a vast amount of evidence that hydrogen bonds have substantial influence on the rheology of polymers. Moreover, low molecular weight products can behave as polymers as a result of cooperative physical interactions arising from hydrogen bonds. However, a clear-cut comparison of the rheology of similar materials with and without hydrogen bonds is still lacking. It is the objective of this work to reveal such differences in order to distinguish between the effects arising from H-bonds and the effects from other physical interactions.

Here we report on the synthesis and rheological characterization of isocyanate functional oligomers that are end-capped with melamine groups. These melamine-urea units can form hydrogen bonds in DADA arrays.

Experimental Part

General Methods and Materials

All reagents were purchased from Aldrich and used as received. Melamine was obtained from DSM and $pTHF_{1000}$ (industrial grade) was obtained from Dupont. All syntheses were performed under a N_2 atmosphere and with mechanical stirring. All glassware was thoroughly dried before starting the reactions.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer. IR spectra were taken on a Perkin Elmer FT-IR spectrometer model System 2000 using a MCT detector. A thin film was pressed between Teflon foils at 90 °C at a pressure of 5 tons. The film was placed between two NaCl windows in a Beckman cell. Transmission spectra were recorded between 21 and 215 °C. DSC traces were obtained with a Perkin Elmer DSC-7 using heating and cooling rates of $10\ K \cdot min^{-1}$. The second heating curve was used to determine the glass transition temperature. Small angle X-ray scattering (SAXS) experiments were performed on a modified Kratky set-up, equipped with an OED50M position sensitive detector (M. Braun) using a line shaped beam profile. The distance between the sample and the detector in these experiments was fixed at 288 mm. The scattering intensities were normalized with respect to a polyethylene standard sample and corrected for the transmission-weighted camera background. De-smearing of the scattering data has been performed using the infinite slit approach of Vonk as implemented in the program FFSAXS. Dielectric measurements were performed on a Novocontrol BDS 40 dielectric analyser with Alpha-analyser in combination with the dielectric sample cell of Novocontrol. The temperature range was between −130 °C and 50 °C with a heating rate of $5\ K \cdot min^{-1}$. A geometric (each time doubling) series of measurement frequencies was selected between 0.125 Hz and 1 MHz.

Mechanical Testing

Sample Preparation

All materials used were thoroughly dried under reduced pressure at 80 °C for at least 24 h before conducting rheological and mechanical tests in order to avoid plasticising effects of water.

Dynamic Mechanical Analysis

The dynamic mechanical properties of the melt were measured with a RDA-2 rheometer from Rheometric Scientific, equipped with either an 8 mm or 25 mm diameter parallel plate measurement geometry. Frequency scans from $\omega = 0.1$ to 100 $rad \cdot s^{-1}$ were recorded at temperatures between 0 °C and 130 °C (at 10 °C intervals). For temperatures above 80 °C, 25 mm plates were used, while for lower temperatures the 8 mm plates were used. To allow thermal equilibration the samples were kept for 7 min at the measurement temperature before starting the frequency sweep. The curves obtained were used to construct master curves with the Time-Temperature-Superposition module of the software package IRIS™.

The dynamic mechanical properties of the solid-state were measured with a Rheometric Scientific Ares system equipped with a rectangular torsion geometry. A sample bar, approximately $12.5 \times 2.0 \times 40$ mm, was subjected to a maximum shear strain of 0.8%. The length, approx. 40 mm, was measured as the distance between the clamps. Measurements were carried out at a constant frequency of 1 Hz during a so-called temperature sweep between −150 °C and 100 °C at a heating rate of $3\ °C \cdot min^{-1}$.

Tensile Testing

The samples were pressed into plates ($100 \times 100 \times 1$ mm) at 100 °C in order to avoid air bubbles. From each plate five dog-bone shaped bars were cut and subjected to stress-strain testing at room temperature. The tensile tests were performed with a Zwick 1445 tensile tester. The elongation was measured with an optical extensometer from Zwick. The force transducer used had a maximum load of 2 000 N and the gauge length was approximately 20 mm. The test speed was set to $20\ mm \cdot min^{-1}$.

Synthesis of (Melamine-IPDI)$_2$-pTHF$_{1000}$ + 0–10 mol-% Hexane Diol (**1a–c**)

To a solution of IPDI (isophorone diisocyanate, 22.2 g, 0.1 mol) in DMSO (75 ml), 6 drops of DBTDL (dibutyltin

dilaureate) were added. Then, $pTHF_{1000}$ (polytetrahydrofuran) and optional 1,6-hexane diol (in total 0.05 mol) dissolved in DMSO (75 ml) were added slowly through a dropping funnel over a time period of 1 h. The mixture was stirred under nitrogen atmosphere for approx. 16 h at room temperature and then another 2 h at 75 °C. Melamine (12.6 g, 0.1 mol) was added and the reaction mixture was stirred for 26 h at 75 °C. DMSO was removed in vacuo at 120 °C and the resulting white product was dried for 48 h at 120 °C under reduced pressure and with N_2 flow. All compounds were obtained as white, flexible materials.

1a ($pTHF_{1000}$: 1,6-hexanediol 100/0)

$T_g = -40$ °C.

^{1}H NMR (DMSO-d_6): $\delta = 9.6$ (bs, 2H, NHCONH-mel), 9.5 (bs, 2H, NHCONH-mel), 7.0 (bs, 8H, NH_2), 6.1 (s, 2H, NHCOO), 4.1 (4H, m, CH_2OCONH), 3.6 (2H, m, CHNHCOO), 3.4 (s, CH_2O polymer), 3.0 (bs, 4H, CH_2NHCONH), 1.7 (s, CH_2CH_2O polymer), 1.3–0.9 (m, CH IPDI).

1b ($pTHF_{1000}$:1,6-hexanediol 95/5)

^{1}H NMR (DMSO-d_6): $\delta = 9.6$ (bs, 2H, NHCONH-mel), 9.5 (bs, 2H, NHCONH-mel), 7.0 (bs, 8H, NH_2), 6.1 (bs, 2H, NHCOO), 4.1 (4H, m, CH_2OCONH), 3.6 (2H, m, CHNHCOO), 3.4 (s, CH_2O polymer + OCH_2 hexane diol), 3.0 (bs, 4H, CH_2NHCONH), 1.7 (s, CH_2CH_2O polymer + OCH_2CH_2 hexane diol), 1.3–0.9 (m, CH IPDI + CH_2 hexanediol).

1c ($pTHF_{1000}$:1,6-hexanediol 90/10)

^{1}H NMR (DMSO-d_6): $\delta = 9.6$ (bs, 2H, NHCONH-mel), 9.5 (bs, 2H, NHCONH-mel), 7.0 (bs, 8H, NH_2), 6.1 (bs, 2H, NHCOO), 4.1 (4H, m, CH_2OCONH), 3.6 (2H, m, CHNHCOO), 3.4 (s, CH_2O polymer + OCH_2 hexane diol), 3.0 (bs, 4H, CH_2NHCONH), 1.7 (s, CH_2CH_2O polymer + OCH_2CH_2 hexane diol), 1.3–0.9 (m, CH IPDI + CH_2 hexanediol).

Synthesis of (Methanol-IPDI$_2$)-pTHF$_{1000}$ (**2**)

To a solution of IPDI (11.1 g, 0.05 mol) in $CHCl_3$ (60 ml), 3 drops of DBTDL were added. Then, $pTHF_{1000}$ (25 g, 0.025 mol) dissolved in $CHCl_3$ (60 ml) was added slowly through a dropping funnel over approximately 30 min. The resulting mixture was stirred for 16 h at room temperature and under nitrogen atmosphere. The mixture was then heated to 60 °C and methanol (1.6 g, 0.05 mol) in $CHCl_3$ (30 ml) was added together with another 3 drops of DBTDL. The reaction mixture was heated under reflux until there was no more isocyanate signal in IR. The $CHCl_3$ was removed in vacuo the product was dried for 2 d at 60 °C under reduced pressure and with N_2 flow.

^{1}H NMR (DMSO-d_6): $\delta = 7.0$ (bs, 4H, NH), 3.9 (m, 6H, OCH_2), 3.6 (d, 6H, OCH_3), 3.4 (s, OCH_2 polymer), 2.7 (d, 4H, CH_2NHCOO), 1.5 (s, OCH_2CH_2 polymer), 1.2–0.9 (m, CH IPDI).

$T_g = -45$ °C.

Synthesis of Poly(Cyclohexanemethanol-IPDI-pTHF$_{1000}$-IPDI) (**3**)

$pTHF_{1000}$ was dried by azeotropic distillation with $CHCl_3$. To a solution of IPDI (5.73 g, 0.0258 mol) in $CHCl_3$ (10 ml), 3 drops of DBTDL were added. Then $pTHF_{1000}$ (12.5 g, 0.0125 mol) in $CHCl_3$ (10 ml) was slowly added and the resulting mixture was left over night at 40 °C. After 21 h reaction at 40 °C, 1,4-cyclohexane dimethanol (1.8 g, 0.0125 mol) in $CHCl_3$ (20 ml) was added and the reaction mixture heated under reflux for 4 h. Then all isocyanate had reacted as evidenced by IR. Subsequently, 0.001 g IPDI was added. IR spectra were recorded after 4 h at 60 °C and then the isocyanate peak was gone. Another 0.001 g IPDI and 2 droplets of catalyst were added and the reaction was left for 16 h at 60 °C. The $CHCl_3$ was evaporated using rotavapour and the reaction continued at 80 °C for 6 h in bulk. The final product was dried at 60 °C for 2 d under reduced pressure and N_2. GPC analysis yielded: $\bar{M}_n \approx 3\,800$ g · mol^{-1} and $\bar{M}_w \approx 17\,000$ g · mol^{-1}.

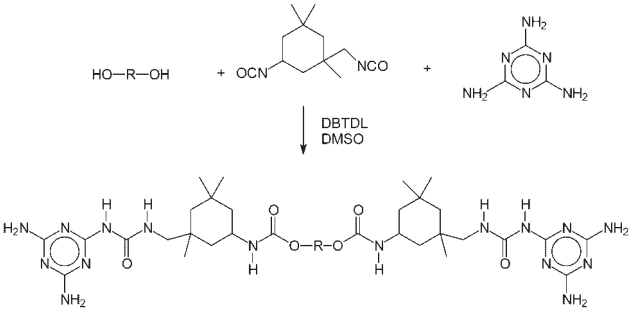
^{1}H NMR (DMSO-d_6): $\delta = 4.8$ (bs, 2H, NHCOO), 4.6 (bs, 2H, NHCOO), 4.0 (bs, OCH_2), 3.9 (bs, CHNHCOO), 3.4 (s, OCH_2 polymer), 2.9 (d, 4H, CH_2NHCOO), 1.6 (s, OCH_2CH_2 polymer), 1.3–0.9 (m, CH IPDI + cyclohexane).

$T_g = -25$ °C.

Results and Discussion

Synthesis of Supramolecular Polymers **1a–c** *and Reference Compounds* **2–3**

Supramolecular polymers **1a–c** have been synthesized in a one pot synthesis by coupling a diol (hydroxyterminated $pTHF_{1000}$ with 0–10 mol-% 1,6-hexanediol) to melamine employing isophorone diisocyanate as the coupling reagent (see Figure 1). It has been shown previously that the primary and secondary isocyanate present in IPDI show different reactivities.[14] In fact, by using dibutyltin dilaureate the reactivity ratio between the primary and secondary isocyanate is approximately 1:10. Reference compound **2**



1a : R = $pTHF_{1000}$

1b : R = $pTHF_{1000}$/1,6-hexanediol 95/5

1c : R = $pTHF_{1000}$/1,6-hexanediol 90/10

Figure 1. Synthesis of the supramolecular polymers **1a–c**.

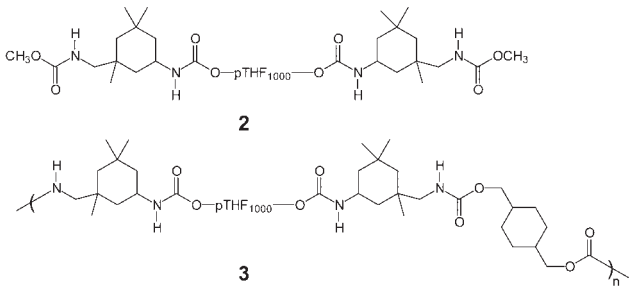


Figure 2. Reference compounds **2** and **3**.

(Figure 2) was prepared in an identical way as **1a**–**c** except that MeOH was used instead of melamine. Finally, a covalently bonded reference polymer **3** (Figure 2) was prepared by chain extending IPDI-pTHF$_{1000}$-IPDI with 1,4-cyclohexane dimethanol.

Frequency Sweep Tests

With the frequency sweep tests the rheological properties of the materials were investigated at temperatures between 0 °C and 130 °C. Figure 3a and b show the dynamic modulus (G_d) and the phase angle (δ) of the supramolecular complex without hexane-diol, at various temperatures. These curves are also typical for the complexes with 5 and 10% hexane diol that only have slightly higher viscosities.

At high temperatures the material has the properties of a Newtonian liquid (phase angle 90 degrees) with moderate viscosity (10–100 Pa · s). At lower temperatures the material becomes elastic, as can be noticed from a decrease of the phase angle. Between 0 °C and 20 °C the material is highly elastic but does not show a well defined minimum in the phase angle, as would be expected for an entangled polymer melt. Moreover, the dynamic shear modulus in this temperature range is exceptionally high for an entanglement network with values of 50–100 MPa. The same was observed for the supra-molecular complexes with 5 and 10% hexane-diol. It is concluded that the materials change with decreasing temperature from a Newtonian fluid to a stiff elastic material.

In order to investigate whether the supra-molecular complex displays thermo-rheological simple behavior we re-plotted the data in a graph of the phase angle versus the dynamic modulus, with the angular frequency as parameter (Figure 4). The data measured at various temperatures are presented with separate curves. This type of plot is known to be temperature invariant in the case of thermo-rheological simple behavior.[15] If the time-temperature superposition (TTS) holds the curves at various temperatures should superimpose into a single mastercurve. From Figure 4 it appears that the supramolecular complex does not show simple behavior. At a fixed value of the dynamic modulus

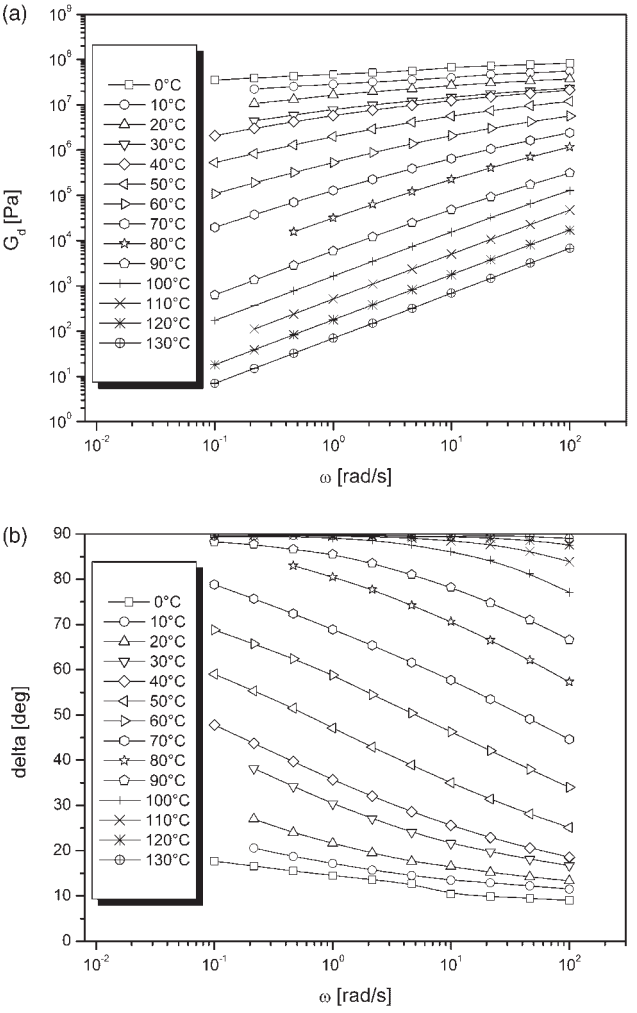


Figure 3. (a) The dynamic modulus of the supra-molecular compound without hexane-diol, at various temperatures, as a function of the angular frequency. (b) The phase angle of the supramolecular compound without hexane-diol, at various temperatures, as a function of the angular frequency.

the phase angle increases with increasing temperature, especially in the temperature interval between 70 °C and 100 °C. This is attributed to a narrowing of the relaxation time spectrum with increasing temperature and indicates that two or more (relaxation) mechanisms with different thermal activation are simultaneously active in this temperature interval. It is concluded that the relaxation curves cannot be attributed solely to reptative or Rouse-like motion, as is the case for covalently bonded linear polymers.

Despite the complex behavior of the supramolecular complex a mastercurve could be constructed at a reference temperature of 80 °C from the frequency sweeps at various temperatures by allowing both horizontal shifts (a_T) along the frequency axis (simple behavior) and vertical shifts along the modulus axis, i.e. so-called thermo-rheological complex behavior. Figure 5 shows the mastercurve and Table 1 the shift factors used in constructing the curve. A

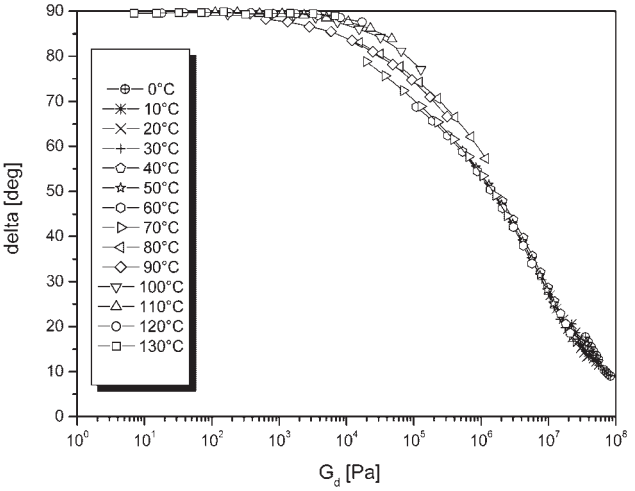


Figure 4. The phase angle versus the dynamic modulus for the supra-molecular compound without hexane-diol, at various temperatures.

considerable shift along the modulus axis (b_T), over slightly more than 1 decade, is required to obtain a mastercurve of good quality. Also the supra-molecular complexes with 5 and 10 mol-% hexane diol display thermo-rheological complex behavior.

Similar frequency scans were performed on the blocked pre-polymer and the covalently bonded material, again at temperatures between 0 °C and 130 °C. These materials show thermo-rheological simple behavior. Good quality mastercurves could be obtained by shifting along the frequency axis only. Figure 6 and 7 show the mastercurves for these two materials. The behavior of both materials is typical of unentangled oligomeric species; like a Newtonian liquid at low frequencies with some elasticity (Rouse modes) at the highest frequencies upon approaching the transition regime. At the reference temperature (80 °C) the viscosities of the covalently bonded material and of the blocked pre-polymer amount to about 130 Pa · s and 15 Pa · s, respectively. These values are significantly lower than the viscosity of the complex without hexane-diol (about 32 kPa · s), and indicate that hydrogen-bonding interactions in the supra-molecular complexes have a dominant effect on the rheological properties. This was further investigated by comparing the temperature dependence of the viscosity of the materials.

Table 1. Horizontal (a_T) and vertical (b_T) shift factors for the supra-molecular complex without hexane-diol.

Temperature °C	log(a_T)	log(b_T)
30	4.22	0.26
40	3.81	0.26
50	2.87	0.28
60	1.98	0.33
70	1.11	0.33
80 (ref)	0	0
90	−0.74	0.04
100	−1.73	−0.38
110	−2.41	−0.53
120	−3.05	−0.70
130	−3.63	−0.88

Flow Activation Energy

From the shift factors obtained in constructing the mastercurves the activation energy of the flow process, assuming Arrhenius behavior, can be calculated according to Equation (1). Since the glass transition temperature for all materials is about −50 to −40 °C, the Arrhenius equation is

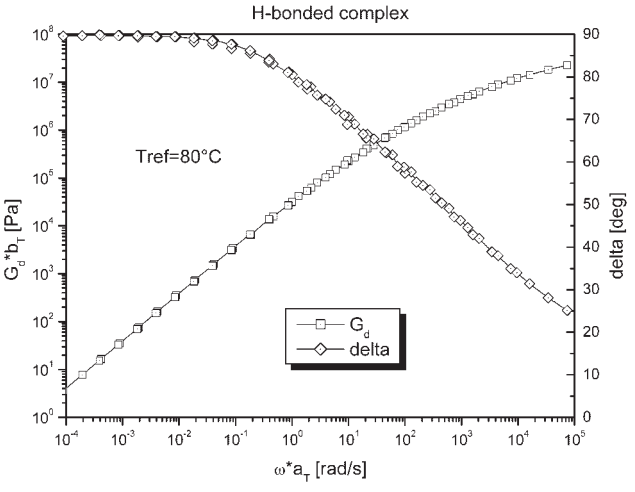


Figure 5. Master-curve at a reference temperature of 80 °C of the supra-molecular compound without hexane-diol.

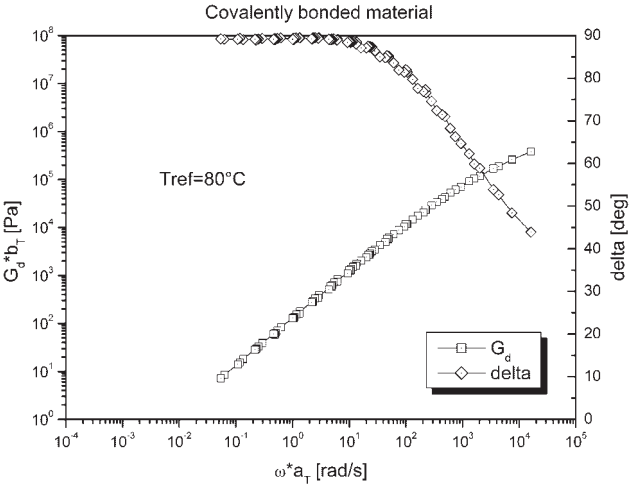


Figure 6. Master-curve at a reference temperature of 80 °C of the covalently bonded material.

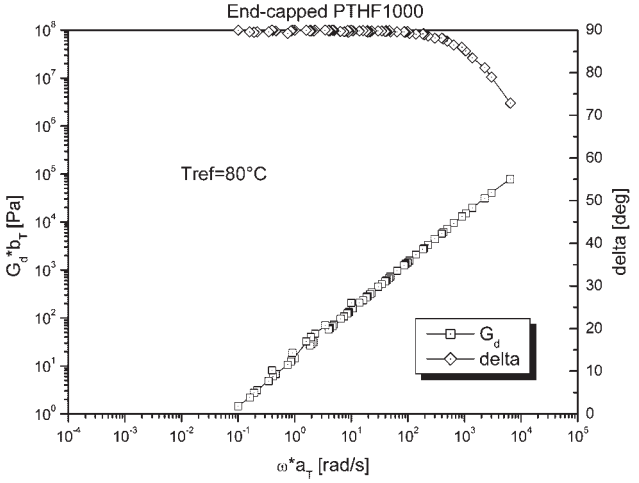


Figure 7. Master-curve at a reference temperature of 80 °C of the low molecular weight blocked pTHF-urethane compound.

expected to apply at temperatures above +50 °C, while at lower temperatures WLF behavior is expected. In Figure 8 the shift factors were plotted versus the reciprocal temperature.

$$\ln(\eta(T)) - \ln(\eta(T_{\mathrm{ref}})) = \ln \mathrm{a}(T) - \ln \mathrm{b}(T) = E_{\mathrm{a}} \times (1/(RT) - 1/(RT_{\mathrm{ref}})) \quad (1)$$

For the non-hydrogen bonding materials the Arrhenius Equation (1) does indeed hold and a straight line in found in Figure 8. At temperatures above 50 °C an activation energy of about 85 kJ · mol^{-1} is found for the covalently bonded material and about 70 kJ · mol^{-1} for the low molecular weight end-capped pre-polymer, respectively. For the supra-molecular complexes the situation is more complicated. The slope of the curve changes at about 100 °C, between 50 and 100 °C it is significantly higher than at

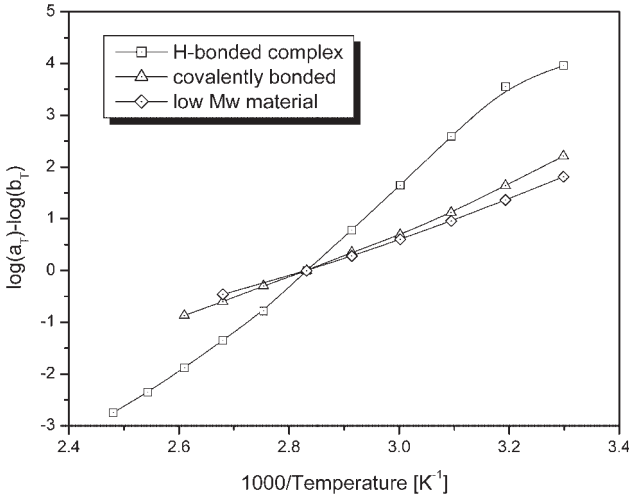


Figure 8. The shift factors of the different materials as a function of 1/*T*.

higher temperatures. In the low temperature interval the activation energy amounts to 180–200 kJ · mol^{-1}, while at higher temperatures the activation energy is less than 100 kJ · mol^{-1}. Therefore, two different activation energies have been calculated, one for the interval 50–100 °C and one above 100 °C and compiled in Table 2.

The higher activation energy corresponds to a stronger temperature dependence of the viscosity and suggests that an additional mechanism is active which causes an additional decrease of the viscosity with increasing temperature. At the highest temperatures the zero-shear viscosity of the complexes approaches zero shear viscosity of the non-hydrogen bonding materials; probably all hydrogen bonds are broken.

DMA in Torsion on the Solid State

From the rheological investigations it was concluded that the supra-molecular complexes show an exceptionally high elastic modulus at temperatures above T_{g}, in combination with a strong temperature dependence of the viscosity at temperatures between 50 °C and 100 °C. In order to investigate this in more detail dynamic measurements were performed in torsion at a fixed frequency of 1 Hz from low temperatures (in the glassy state) up to the temperatures at which the rheological measurements were performed. Figure 9 contains the DMA curves, both the dynamic modulus G_{d} and the tangent of the phase angle tan(δ), for the three supra-molecular compounds as a function of temperature.

At the lowest temperatures the materials have a typical glassy shear modulus of about 2 GPa. With increasing temperature, the modulus decreases and a weak maximum in the loss tangent occurs around −125 °C. This glassy state relaxation process is attributed to local motions in the pTHF chain segments.[16] Around −50 °C a shoulder is found in the loss tangent, accompanied by a decrease of the modulus over about 1 decade. This relaxation process is attributed to the glass transition, which was substantiated by DSC measurements. For the supra-molecular complexes in this study the glass transition appears to be very broad and relatively weak. Finally, above T_{g} the modulus decreases gradually with further increasing temperature.

In a pure amorphous material a steep drop of the modulus at the glass transition is expected. This is not the case for the supra-molecular compounds studied. In view of both the broadness of the glass transition and the modulus values at temperatures between T_{g} and 50 °C, the curves are similar to those of a typical semi-crystalline polymer. However, for a semi-crystalline polymer a steep drop in modulus due to melting is expected at higher temperatures. This is not the case for the supra-molecular complexes, no clear melting point is observed and, instead, a gradual decrease of the modulus occurs. Above 50 °C the loss tangent passes the G′-G″ crossover (tan$\delta = 1$) and the material gradually

Table 2. Flow activation energy and zero shear viscosity at $T_{ref} = 80\,^{\circ}C$ of the various materials.

Material	E_a	η_0 (80 °C)	
	kJ · mol^{-1}		
Supra-molecular compounds	180–200	0% hexane diol	40 kPa · s
50 °C < T < 100 °C		5% hexane diol	100 kPa · s
Supra-molecular compounds T > 100 °C	<100	10% hexane diol	100 kPa · s
Covalently bonded material	85	130 Pa · s	
End-capped pTHF prepolymer	70	15 Pa · s	

changes into a liquid. Again, these results are in agreement with DSC measurements that revealed no melting peak or crystallization phenomena above T_g.

These findings can be explained by assuming that, in addition to hydrogen bonding between the building blocks (thus forming a supramolecular linear chain), the material phase separates. Hard-soft block phase separation is often found for urethane polymers and might be operative in our systems as well. The complexes with 5 or 10% hexane diol have a higher (melamine) hard block content, which is reflected in higher values of the dynamic modulus.

Mechanical Properties

The mechanical properties of the supra-molecular complexes containing 0, 5 and 10% 1,6-hexanediol, were investigated. The tensile stress-strain behavior of the sample bars, at room temperature, is shown in Figure 10.

The materials show tough deformation behavior. After passing a yield point large-scale plastic flow occurs. The modulus and the yield stress increase with increasing hexane-diol content while the behavior becomes more brittle. The fracture strain decreases from more than 100 to 30%. It is remarkable that all materials show strain softening despite the fact that the measurements are performed above T_g. All samples deform homogeneously and no necking was observed. The strain softening is thought to be a consequence of breaking of hard domains and/or hydrogen bonds during testing.

Structural Investigation

From the mechanical and rheological properties of the materials it was deduced that the supra-molecular complexes are most probably phase-separated and contain a fraction of hard domains. However, DSC traces only revealed a broad glass transition between −60 and −20 °C, and no indications for melting of domains in the complexes. In order to further investigate this dielectric and small angle X-ray scattering (SAXS) experiments were performed.

Figure 11a and b show the dielectric constant and the dielectric loss index of the supra-molecular complex without hexane-diol, at various frequencies, as a function of temperature. Similar to the DMTA results, the β-transition is found at very low temperatures (below −100 °C), which is again attributed to a local mechanism of motion in the pTHF chain segments.[16] Around −50 °C a stronger relaxation process, the α-transition, is found that is as in the mechanical case attributed to the glass transition. With further increasing temperature the dielectric losses increase

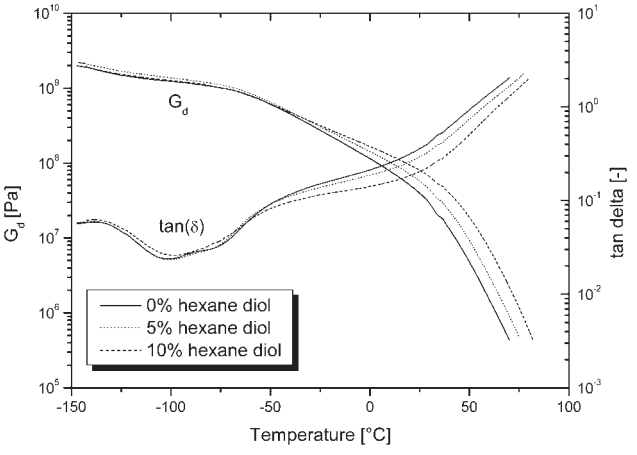


Figure 9. Dynamic mechanical properties at low temperatures (solid-state) of the three supra-molecular complexes.

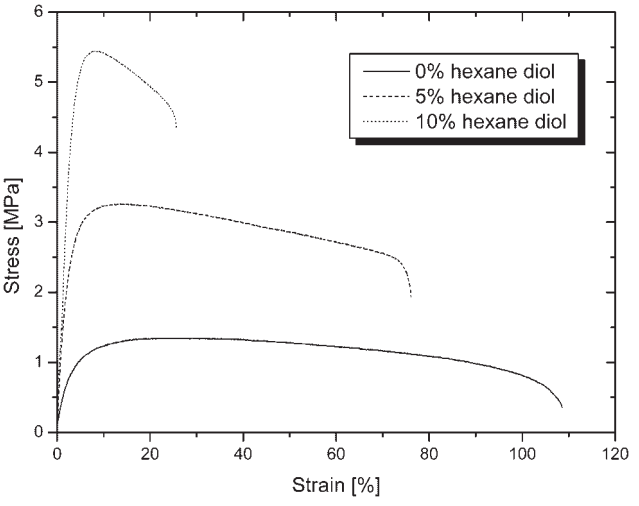


Figure 10. Stress-strain curves for the different supra-molecular complexes at room temperature.

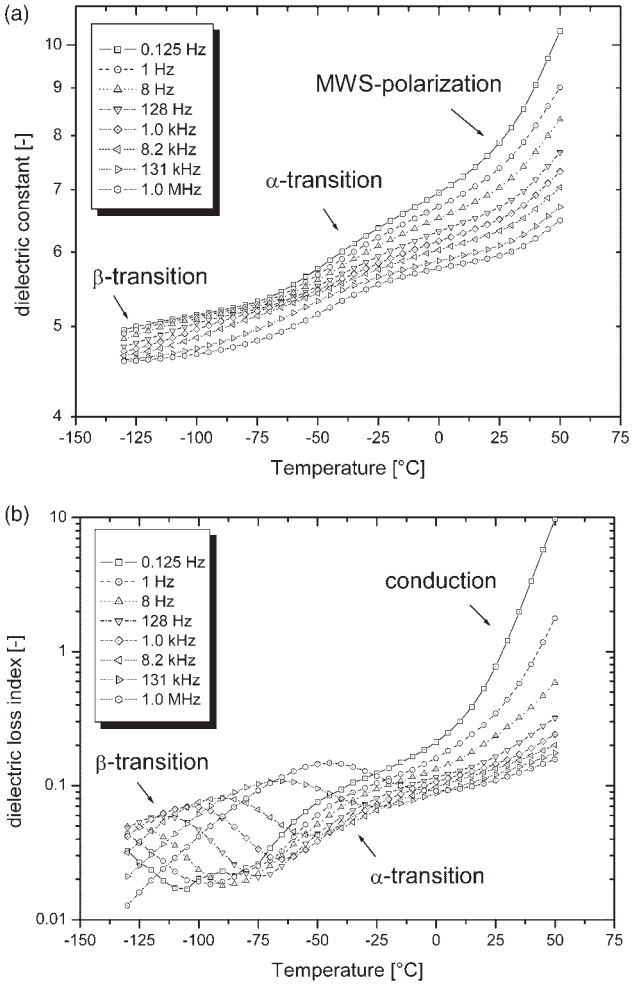


Figure 11. (a) The dielectric constant of the supra-molecular complex without hexane diol, at various frequencies, as a function of temperature; (b) The dielectric loss index of the supra-molecular complex without hexane diol, at various frequencies, as a function of temperature.

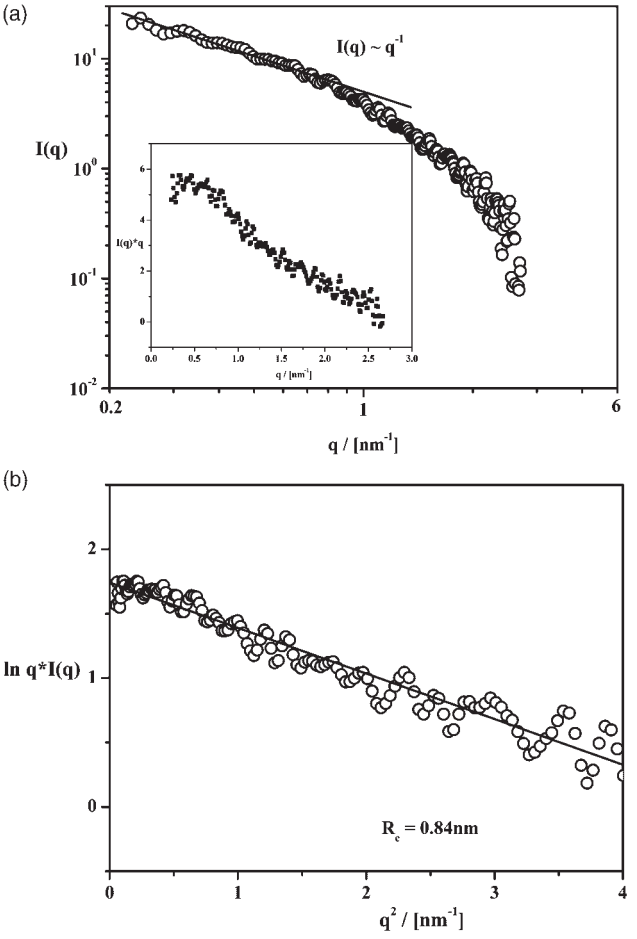


Figure 12. (a) SAXS pattern of the supra-molecular complex without hexane-diol at room temperature; (b) Guinier plot of the SAXS data.

due to ionic conduction, which is usually the case for polar materials above the glass transition. However, at the same time the dielectric constant increases. Except for possible electrode polarization at very high ionic conduction, such an increase is not expected for a homogenous material. Often, polarization mechanisms above T_g can be attributed to a so-called Maxwell-Wagner-Sillars (MWS) process as a consequence of interfacial polarization.[17] In heterogeneous materials, e.g. semi-crystalline polymers, MWS polarization usually occurs in the rubbery state due to blocking of charge carrier transport at the interfaces between the conductive amorphous phase and the non-conductive crystallites.[18] The supra-molecular complexes show similar behavior, indicating that the materials are phase separated.

The SAXS patterns recorded from all the systems reveal a diffuse scattering signal at low angles, which is related to the presence of the supramolecular complexes, as can be seen from Figure 12a. The scattering intensity at low angles reveals a decay according to $I(q) \propto q^{-1}$, a behavior which strongly suggest the formation of rod-like assemblies. This is apparent from the Holtzer-plot representation of the scattering data (insert in Figure 12a, $q \cdot I(q)$ vs. q). The plateau at low q values moreover indicates that the height of the supramolecular assemblies exceeds the dimensions corresponding to the instrumental resolution. Although no side maximum of the form factor could be detected in the present experiments, the dimensions of the cross section of the rod-like assemblies can be estimated from the Guinier plot representation displayed in Figure 12b. The latter suggests a Guinier diameter around 0.8–1 nm for all the systems, which can be extracted from the slope of the curve.[19] This value roughly corresponds to the size of the hydrogen-bonded melamine units of the complexes.

It is concluded that both the dielectric and the SAXS results point in the direction that the supramolecular complexes are heterogeneous materials as a consequence

of hard (melamine-urea units) – soft (polyether) block phase separation. It is concluded that the properties of the supramolecular complexes are a result of this phase-separated structure, and its disintegration with increasing temperature. Their mechanical properties show similarity to what is often observed for hard-soft block phase separating polyurethanes.

However, low molecular weight polyurethanes with acceptable mechanical properties are not known. To attribute the physical and mechanical properties solely to phase separation seems not appropriate. Only the low molecular supramolecular materials of Meijer et al.[10] have, to best of our knowledge, comparable mechanical properties as our materials. Therefore, we strongly believe that the hydrogen bonding represents a substantial part of the physical interaction.

Conclusions

Despite the low molecular weight of the structural units of the melamine-based pTHF-urethane supra-molecular complexes (less than 2 000 $g \cdot mol^{-1}$) the complexes show high molar mass polymeric properties. The complexes have a much higher viscosity than both the blocked pre-polymer and the covalently bonded polymer based on these units. Moreover, the supra-molecular compounds show a stronger temperature dependency of the viscosity. No clear entanglement plateau is found; with increasing temperature the materials gradually relax from the glassy state into flow with remarkably high values for the modulus after passing the glass transition. The behavior of the complexes is similar to that of high molecular weight semi-crystalline materials.

Tough DSC experiments did not show any signs for melting or crystallization, dielectric and small angle X-ray (SAXS) measurements revealed that the materials are heterogeneous, consisting of an amorphous phase containing highly ordered cylindrically shaped domains.

This heterogeneous structure has a significant influence on the mechanical behavior of the materials at room temperature, which changes from soft and tough to hard and more brittle upon increasing the hard block content by exchanging a fraction of the pTHF chains with the much lower molecular weight hexane diol.

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